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Published in:
The Journal of Chemical Physics

DOI:
[10.1063/5.0002389](https://doi.org/10.1063/5.0002389)

Publication date:
2020

Document version
Peer reviewed version

Citation for published version (APA):
Schnack-Petersen, A. K., Simmermacher, M., Fasshauer, E., Jensen, H. J. A., & Sauer, S. P. A. (2020). The Second-Order-Polarization-Propagator Approximation SOPPA in a Four Component Spinor Basis. *The Journal of Chemical Physics*, 152, [134113]. <https://doi.org/10.1063/5.0002389>

The Second-Order-Polarization-Propagator- Approximation SOPPA in a Four-Component Spinor Basis

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Abstract

A theoretical framework for understanding molecular structures is crucial for the development of new technologies such as catalysts or solar cells. Apart from electronic excitations energies however, only spectroscopic properties of molecules consisting of lighter elements can be computationally described at high level of theory today, since heavy elements require a relativistic framework and most methods have only been derived in a non-relativistic one so far. Important new technologies like the above mentioned require molecules that contain heavier elements and hence there is a great need for the development of relativistic computational methods at higher level of accuracy.

Here, the Second-Order-Polarization-Propagator-Approximation (SOPPA), which has proven very successful in the non-relativistic case, is adapted to a relativistic framework. The equations for SOPPA are presented in their most general form, i.e., in a non-canonical spin-orbital basis, which can be reduced to the canonical case, and the expressions needed for a relativistic four-component SOPPA are obtained. The equations are one-index transformed, giving more compact expressions that correspond to those already available for the four-component RPA. The equations are ready for implementation in a four-component quantum chemistry program, which will allow both linear response properties and excitation energies to be calculated relativistically at the SOPPA level.

Introduction

The development of new and better technologies requires a thorough understanding of the molecules, whose properties one wishes to exploit. Such an understanding is greatly reliant on understanding molecular electronic structures, which various spectroscopic methods can explore. Unfortunately, interpretation of the experimental data is not always straightforward. Often the extraction of information relies heavily on empirical models, the viability of which is limited to classes of molecules that can be assumed to show similar properties when elements of the same types are found in similar environments. This method becomes unreliable when molecules with very different structures are investigated, which is the case for e.g., metalloproteins¹⁻⁴. Here, theoretical approaches are needed for reference spectra, which naturally necessitates accurate, yet computationally feasible methods. Spectroscopic parameters can be determined using linear response theory, where the parameters are calculated from the response of a system to a perturbation by an external electromagnetic field. Many approaches based on the non-relativistic electronic Schrödinger equation, where the speed of light is assumed infinite and where the electrons are thus considered non-relativistically, exist for lighter atoms. Especially the Second-Order-Polarization-Propagator-Approximation

(SOPPA)⁵ has proven very useful, as it yields results in good agreement with experiment, while being computationally less demanding than the high-accuracy Coupled Cluster (CC) methods⁶. For larger systems of more than roughly 30 atoms or 800 basis functions, however, even SOPPA can be rather time consuming, wherefore cheaper, but also less reliable alternatives are available such as RPA^{7,8}, RPA(D)^{9–11}, HRPA¹² and HRPA(D)^{9,10}. In addition to the abovementioned methods, a range of TDDFT methods are also available¹³. For TDDFT, however, it is difficult to predict the reliability of a method outside of a certain set of molecules and properties for which a given functional has been optimized¹⁴.

Two other second-order-methods have been formulated and implemented for non-relativistic calculations of excitation energies or linear response properties: ADC(2)^{15,16} and CC2¹⁷. For non-relativistic calculations of excitation energies and polarizabilities the performance of these three methods and their implementations has frequently been compared.^{18–23} In contrast, for spin-spin couplings, only two comparisons for small inorganic molecules have been published so far: one between SOPPA and CC2²⁴ and one between SOPPA and ADC(2),²⁵ in which also the first non-relativistic implementation of ADC(2) for spin-spin coupling constants was presented.

For heavy elements the available methods based on the Schrödinger equation often become insufficient. Heavy elements are interesting both as central components in catalysts^{26,27} as well as solar cells²⁸ and as highly toxic pollutants that need to be removed from the environment²⁹. Due to larger nuclear charges, electrons close to the nucleus can move at speeds close to that of light, giving rise to relativistic effects such as spin-orbit coupling, the Darwin term (from a relativistic fluctuation of an electron about its mean position³⁰), and the mass-velocity correction, which can all severely affect spectroscopic properties. Effects on NMR parameters, for instance, can already be observed for the third period of the periodic table^{31,32}. For one-bond couplings between Se and other elements, the relativistic corrections were estimated to constitute 10%–60% of the total indirect nuclear spin-spin coupling constant^{30,33} and for the Se-Se coupling the effect was 170% due to a wrong sign from the

non-relativistic calculation, which demonstrates that performing such calculations at a non-relativistic level of theory makes no sense³⁰. Similarly, relativistic effects have been estimated to constitute approximately 15% of the total indirect spin-spin coupling constants between Te and H³⁴. A popular approach for the calculations of coupling constants is thus to amend non-relativistic SOPPA calculations with relativistic corrections obtained from 4-component TDDFT calculations^{30,33,34}. The fairly large contribution from relativistic effects indicated by this mixture of methods, however, implies the need for a 4-component version of SOPPA. By using methods based on the Dirac equation (relativistic methods), relativistic effects can be included. In principle one can derive the same methods in the relativistic framework as in the non-relativistic one. This, however, requires equations to be given in a spin-orbital basis, as spin is included in the relativistic Hamiltonian and therefore cannot be integrated out of the equations. Due to the increased computational costs, the number of available methods is rather limited. So far, only RPA, which is merely time-dependent Hartree-Fock (TD-HF), as well as TDDFT methods are available for fully relativistic calculations of general linear response properties^{35–38}, although more four-component methods exist for calculations of excitation energies: ADC(2)^{39,40} and equation-of-motion CCSD⁴¹. The available RPA is, at least in its non-relativistic form, considered inadequate, as it includes little electron correlation and is prone to triplet instabilities, wherefore it is also likely to be insufficient in the relativistic case. The relativistic ADC(2) may be reformulated and implemented to allow for the calculation of general linear response properties.

In this article the equations needed for a four-component SOPPA are presented. As SOPPA has proven very useful in the non-relativistic case⁶, in particular for NMR properties we expect it to prove equally powerful and relevant under relativistic conditions. This article starts by briefly introducing the reader to the linear response equations as well as to the equations needed for the determination of excitation energies. Then follows a section devoted to the derivation of the SOPPA equations in the non-canonical spin-orbital basis applicable to both non-relativistic, two-component, and full four-component implementa-

tions. The third section discusses suitable strategies for reducing computational costs of an implementation of these equations in a relativistic code. The linear transformation of trial vectors as well as the one-index transformation of the equations needed for computationally efficient implementation of SOPPA are presented in the fourth section. Finally, the fifth section outlines a possible approach for an implementation of the equations.

1 Theory

1.1 Linear Response Theory

Linear response properties are defined by the perturbation expansion of the expectation value of a property, P . For a system perturbed by a time-dependent field, $\mathcal{F}(t')$, with components $\mathcal{F}_\beta(t')$, this expansion is⁴²

$$\langle \Psi_0(t, \mathcal{F}) | \hat{P} | \Psi_0(t, \mathcal{F}) \rangle = \langle \Psi_0 | \hat{P} | \Psi_0 \rangle + \int_{-\infty}^{\infty} dt' \sum_{\beta} \langle \langle \hat{P}; \hat{O}_{\beta}^I(t' - t) \rangle \rangle \mathcal{F}_{\beta}(t') + \dots \quad (1)$$

In the above, $|\Psi_0\rangle$ denotes the time-independent and unperturbed field-free reference state, while $|\Psi_0(t, \mathcal{F})\rangle$ is the time-dependent and perturbed wavefunction. Furthermore, \hat{P} is the operator representing the given property, while $\sum_{\beta} \hat{O}_{\beta} \mathcal{F}_{\beta}(t')$ is the first order correction to the field-free Hamiltonian, \hat{H}_0 , representing the interaction of the molecule with the field⁴². Eq. (1) is however, formulated in the interaction picture, where the operators, and not the unperturbed wavefunction, carry the time-dependence⁴², and hence, the operator \hat{O}_{β} has been rewritten as $\hat{O}_{\beta}^I(t' - t)$.

The linear response of the property, P , is defined as the second-term on the right hand side of Eq. (1), i.e., the term linear in the perturbing field, and the quantity $\langle \langle \hat{P}; \hat{O}_{\beta}^I(t' - t) \rangle \rangle$ is called the linear response function or the polarization propagator, here shown in the time domain.

Expressions for the linear response function can be derived in numerous ways. One intuitive

way of carrying out this derivation is presented by Olsen et al.^{43,44} as well as by Fuchs et al.⁴⁵ Note that the expression is transformed from the time- to the frequency domain in order to obtain results in the same domain as the experimental data. Using this approach one finds that the linear response function of the operators \hat{P} and \hat{O} can be written in the compact matrix form in atomic units (see e.g., Chapter 7 in Ref. [42]),

$$\langle\langle\hat{P};\hat{O}\rangle\rangle_{\omega} = \mathbf{T}(\hat{P})^T (\omega\mathbf{S} - \mathbf{E})^{-1} \mathbf{T}(\hat{O}) \quad (2)$$

with the matrix elements of the molecular Hessian, \mathbf{E} , and the overlap matrix, \mathbf{S} ,

$$E_{ij} = \langle\Psi_0 | [\hat{h}_i, [\hat{H}_0, \hat{h}_j]] | \Psi_0\rangle \quad (3)$$

$$S_{ij} = \langle\Psi_0 | [\hat{h}_i, \hat{h}_j] | \Psi_0\rangle \quad (4)$$

and the property gradient vectors,

$$\mathbf{T}(\hat{P})^T = \langle\Psi_0 | [\hat{P}, \hat{\mathbf{h}}^T] | \Psi_0\rangle \quad (5)$$

$$\mathbf{T}(\hat{O}) = \langle\Psi_0 | [\hat{\mathbf{h}}, \hat{O}] | \Psi_0\rangle \quad (6)$$

We note that the two property gradient vectors in Eqs. (5) and (6) have the same form. Here, $\hat{\mathbf{h}}$ denotes the vector of excitation operators containing all possible excitations and de-excitations.

The expression in Eq. (2) is generally solved not by evaluating the inverse of $\mathbf{E} - \omega\mathbf{S}$ but by first iteratively solving the inhomogeneous system of equations,

$$(\omega\mathbf{S} - \mathbf{E}) \mathbf{X} = \mathbf{T}(\hat{O}) \quad (7)$$

for the solution vector \mathbf{X} and then determining $\langle\langle\hat{P};\hat{O}\rangle\rangle_{\omega}$ as the product of the property gradient, $\mathbf{T}(\hat{P})$, and \mathbf{X} .

In polarization propagator theory excitation energies are determined by finding the poles of $\langle\langle\hat{P};\hat{O}\rangle\rangle_{\omega}$. This is done by considering the homogeneous problem rather than the inhomogeneous one, namely

$$\mathbf{E}\mathbf{X} = \omega\mathbf{S}\mathbf{X} \quad (8)$$

The excitation energies can then be found as the eigenvalues, ω , of the problem. As can be seen in Eqs. (7) and (8), the molecular Hessian, \mathbf{E} , and the overlap matrix, \mathbf{S} , are needed for both the linear response properties and the excitation energies, while the property gradient vectors, \mathbf{T} , are only required when determining linear response properties or transition dipole moments.

For practical purposes, Eqs. (7) and (8) cannot be solved exactly. The wavefunction, for instance, must be truncated and not all excitations can be included. In the Second-Order-Polarization-Propagator-Approximation (SOPPA)⁵ only single and double excitation and de-excitation operators are considered. In addition, the wavefunction is truncated at second order in perturbation theory and so the second-order Møller-Plesset (MP2) wavefunction, $|\Psi^{\text{MP2}}\rangle$, is chosen as the reference state, $|\Psi_0\rangle$. It turns out that the \mathbf{E} and \mathbf{S} matrix elements that include the second-order contribution to the wavefunction are zero. Hence, only the MP-wavefunction truncated at first order (MP1) is actually needed for the \mathbf{E} and \mathbf{S} matrix elements, while the single excitation part of the MP2-wavefunction is needed for the elements of the property gradient vectors, \mathbf{T} . This gives rise to a linear response function of the

following form

$$\langle\langle\hat{P};\hat{O}\rangle\rangle_{\omega}^{\text{SOPPA}} = \begin{pmatrix} {}^e\mathbf{T}(\hat{P})^{T(0,2)} & {}^d\mathbf{T}(\hat{P})^{T(0,2)} & {}^{ee}\mathbf{T}(\hat{P})^{T(1)} & {}^{dd}\mathbf{T}(\hat{P})^{T(1)} \end{pmatrix} \begin{pmatrix} {}^e\mathbf{X} \\ {}^d\mathbf{X} \\ {}^{ee}\mathbf{X} \\ {}^{dd}\mathbf{X} \end{pmatrix} \quad (9)$$

Here, the left superscripts label the different parts of the vectors corresponding to single (de-)excitations, e (d), and double (de-)excitations, ee (dd). The inhomogeneous system of equations given in Eq. (7) becomes:

$$\begin{aligned} & \left(\omega \begin{pmatrix} \Sigma^{(0,2)} & 0 & 0 & 0 \\ 0 & -\Sigma^{(0,2)*} & 0 & 0 \\ 0 & 0 & \mathbf{1} & 0 \\ 0 & 0 & 0 & -\mathbf{1} \end{pmatrix} - \begin{pmatrix} \mathbf{A}^{(0,1,2)} & \mathbf{B}^{(1,2)} & \tilde{\mathbf{C}}^{(1)} & 0 \\ \mathbf{B}^{(1,2)*} & \mathbf{A}^{(0,1,2)*} & 0 & \tilde{\mathbf{C}}^{(1)*} \\ \mathbf{C}^{(1)} & 0 & \mathbf{D}^{(0)} & 0 \\ 0 & \mathbf{C}^{(1)*} & 0 & \mathbf{D}^{(0)*} \end{pmatrix} \right) \begin{pmatrix} {}^e\mathbf{X} \\ {}^d\mathbf{X} \\ {}^{ee}\mathbf{X} \\ {}^{dd}\mathbf{X} \end{pmatrix} \\ & = \begin{pmatrix} {}^e\mathbf{T}(\hat{O})^{(0,2)} \\ {}^d\mathbf{T}(\hat{O})^{(0,2)} \\ {}^{ee}\mathbf{T}(\hat{O})^{(1)} \\ {}^{dd}\mathbf{T}(\hat{O})^{(1)} \end{pmatrix} \end{aligned} \quad (10)$$

with elements

$$A_{ai,bj}^{(0,1,2)} = \langle \Psi^{\text{MP1}} | [\hat{q}_{ai}, [\hat{H}_0, \hat{q}_{bj}^\dagger]] | \Psi^{\text{MP1}} \rangle^{(0,1,2)} \quad (11)$$

$$B_{ai,bj}^{(1,2)} = \langle \Psi^{\text{MP1}} | [\hat{q}_{ai}, [\hat{H}_0, \hat{q}_{bj}]] | \Psi^{\text{MP1}} \rangle^{(1,2)} \quad (12)$$

$$\tilde{C}_{aibj,ck}^{(1)} = \langle \Psi^{\text{MP1}} | [\hat{q}_{ai}^\dagger \hat{q}_{bj}^\dagger, [\hat{H}_0, \hat{q}_{ck}]] | \Psi^{\text{MP1}} \rangle^{(1)} \quad (13)$$

$$C_{ck,aibj}^{(1)} = \langle \Psi^{\text{MP1}} | [\hat{q}_{ck}^\dagger, [\hat{H}_0, \hat{q}_{ai} \hat{q}_{bj}]] | \Psi^{\text{MP1}} \rangle^{(1)} \quad (14)$$

$$D_{aibj,ckdl}^{(0)} = \langle \Psi^{\text{MP1}} | [\hat{q}_{ai}^\dagger \hat{q}_{bj}^\dagger, [\hat{H}_0, \hat{q}_{ck} \hat{q}_{dl}]] | \Psi^{\text{MP1}} \rangle^{(0)} \quad (15)$$

$$\Sigma_{ai,bj}^{(0,2)} = \langle \Psi^{\text{MP1}} | [\hat{q}_{ai}, \hat{q}_{bj}^\dagger] | \Psi^{\text{MP1}} \rangle^{(0,2)} \quad (16)$$

$${}^{\text{d}}T(\hat{P})_{ai}^{(0,2)*} = {}^{\text{e}}T(\hat{P})_{ai}^{(0,2)} = \langle \Psi^{\text{MP2}} | [\hat{P}, \hat{q}_{ai}^\dagger] | \Psi^{\text{MP2}} \rangle^{(0,2)} \quad (17)$$

$${}^{\text{d}}T(\hat{O})_{ai}^{(0,2)*} = {}^{\text{e}}T(\hat{O})_{ai}^{(0,2)} = \langle \Psi^{\text{MP2}} | [\hat{q}_{ai}, \hat{O}] | \Psi^{\text{MP2}} \rangle^{(0,2)} \quad (18)$$

$${}^{\text{dd}}T(\hat{P})_{aibj}^{(1)*} = {}^{\text{ee}}T(\hat{P})_{aibj}^{(1)} = \langle \Psi^{\text{MP2}} | [\hat{P}, \hat{q}_{ai}^\dagger \hat{q}_{bj}^\dagger] | \Psi^{\text{MP2}} \rangle^{(1)} \quad (19)$$

$${}^{\text{dd}}T(\hat{O})_{aibj}^{(1)*} = {}^{\text{ee}}T(\hat{O})_{aibj}^{(1)} = \langle \Psi^{\text{MP2}} | [\hat{q}_{ai} \hat{q}_{bj}, \hat{O}] | \Psi^{\text{MP2}} \rangle^{(1)} \quad (20)$$

where \hat{q}_{ai}^\dagger and \hat{q}_{ai} are single excitation and de-excitation operators that move an electron from an occupied orbital i to a virtual orbital a and vice versa, respectively. Following a common convention of electronic structure theory, orbitals with indices i, j, k, l, m , and n denote orbitals occupied in the Hartree-Fock wavefunction, while orbitals a, b, c, d, e , and f are unoccupied. The right superscripts, (...), denote the order of the matrix and vector elements in Møller-Plesset perturbation theory.

1.2 Relativistic considerations

The expressions given in Section 1.1 are valid in both the relativistic as well as in the non-relativistic framework, as can be seen from the generic form of the Hamiltonian in second quantization:

$$\hat{H} = \sum_{pq} h_{pq} \hat{a}_p^\dagger \hat{a}_q + \frac{1}{2} \sum_{pqrs} g_{pqrs} \hat{a}_p^\dagger \hat{a}_r^\dagger \hat{a}_s \hat{a}_q \quad (21)$$

where h_{pq} and g_{pqrs} are one- and two-electron integrals, respectively, and \hat{a}_p^\dagger is a creation operator that creates an electron in spin-orbital/spinor p , while \hat{a}_q is an annihilation operator that removes an electron from spin-orbital/spinor q . Together they constitute an excitation (or de-excitation) operator, $\hat{q}_{pq}^\dagger = \hat{a}_p^\dagger \hat{a}_q$ (or $\hat{q}_{pq} = \hat{a}_q^\dagger \hat{a}_p$). The indices p, q, r, s, \dots denote general orbitals that may be both occupied or virtual.

In contrast to the non-relativistic Hamiltonian, however, the relativistic Hamiltonian is a 4×4 matrix for each one-electron term and a 16×16 for each two-electron term. Hence, in the relativistic case, the one-electron wavefunction must be replaced by a spinor, i.e., the description of an orbital must now incorporate spin-orbit coupling. In the fully relativistic case, this spinor is a four-component vector

$$|\psi\rangle = \begin{pmatrix} |\psi^L\rangle & |\psi^S\rangle \end{pmatrix}^T = \begin{pmatrix} |\psi^{L,\alpha}\rangle & |\psi^{L,\beta}\rangle & |\psi^{S,\alpha}\rangle & |\psi^{S,\beta}\rangle \end{pmatrix}^T \quad (22)$$

The first two components on the RHS of Eq. (22) are known as the upper or large components and are therefore labelled L, while the other two components are known as the lower or small components, wherefore they are labelled S. Finally, α and β refer to the spin of the electron.⁴⁶ For systems of more than one electron, the many-electron wavefunction must be considered. The latter is written as a direct product of one-electron spinors and thus, for example, a two-electron wavefunction takes the form⁴⁷

$$|\Psi_{jk}\rangle = |\psi_j\rangle \otimes |\psi_k\rangle = \begin{pmatrix} |\psi_j^{L,\alpha}\rangle \cdot |\psi_k\rangle \\ |\psi_j^{L,\beta}\rangle \cdot |\psi_k\rangle \\ |\psi_j^{S,\alpha}\rangle \cdot |\psi_k\rangle \\ |\psi_j^{S,\beta}\rangle \cdot |\psi_k\rangle \end{pmatrix} = \begin{pmatrix} |\psi_j^{L,\alpha}\rangle |\psi_k^{L,\alpha}\rangle & |\psi_j^{L,\alpha}\rangle |\psi_k^{L,\beta}\rangle & |\psi_j^{L,\alpha}\rangle |\psi_k^{S,\alpha}\rangle & |\psi_j^{L,\alpha}\rangle |\psi_k^{S,\beta}\rangle \\ |\psi_j^{L,\beta}\rangle |\psi_k^{L,\alpha}\rangle & |\psi_j^{L,\beta}\rangle |\psi_k^{L,\beta}\rangle & |\psi_j^{L,\beta}\rangle |\psi_k^{S,\alpha}\rangle & |\psi_j^{L,\beta}\rangle |\psi_k^{S,\beta}\rangle \\ |\psi_j^{S,\alpha}\rangle |\psi_k^{L,\alpha}\rangle & |\psi_j^{S,\alpha}\rangle |\psi_k^{L,\beta}\rangle & |\psi_j^{S,\alpha}\rangle |\psi_k^{S,\alpha}\rangle & |\psi_j^{S,\alpha}\rangle |\psi_k^{S,\beta}\rangle \\ |\psi_j^{S,\beta}\rangle |\psi_k^{L,\alpha}\rangle & |\psi_j^{S,\beta}\rangle |\psi_k^{L,\beta}\rangle & |\psi_j^{S,\beta}\rangle |\psi_k^{S,\alpha}\rangle & |\psi_j^{S,\beta}\rangle |\psi_k^{S,\beta}\rangle \end{pmatrix} \quad (23)$$

Hence, an N -electron wavefunction will have the dimension 4×4^N .

Also note that the expressions given in Section 1.1 as well as in the following are not only general with respect to the choice of the wavefunction and Hamiltonian, but also with respect to

the operators, \hat{P} and \hat{O} , which have generic forms in second quantization as the Hamiltonian in Eq. (21). In the relativistic case one might therefore use the same equations regardless of whether the electron-electron interaction term is the simple Coulomb interaction or if it contains either the Breit- or Gaunt-interaction terms, which are corrections accounting for the retardation effect, arising from the finite speed of light.

Note that not only eigenstates with positive energies that correspond to electronic-electronic orbital rotations are obtained from solving the Dirac equation but also eigenstates with negative energies that correspond to electronic-positronic orbital rotations. To permit the usage of variational methods that minimise the electronic energy, it might therefore be necessary to invoke the no-pair approximation where all states corresponding to eigenstates with negative energies are projected out⁴⁶. An alternative to this approach is utilizing the minimax principle, where the energy is minimized with respect to the large component and maximized with respect to the small component⁴⁸. The latter approach is utilized in, for instance, the relativistic DIRAC code⁴⁹. It is useful because these eigenstates with negative energies are required for a correct description of several properties. Among them are diamagnetic contributions to linear response properties such as NMR coupling constants⁵⁰. It has been found that it is sufficient, at least for couplings between lighter elements, to approximate the diamagnetic contribution to these NMR coupling constants by non-relativistic expressions^{50,51}. Discrepancies between results obtained with these approximations and fully relativistic methods are, however, seen when heavier elements are involved⁵⁰. Another description of the diamagnetic term was proposed by Kutzelnigg⁵², who added a relativistic term to the non-relativistic expression. Once again, this expression is independent of the eigenstates with negative energies. Whether one utilizes the no-pair approximation or not, avoiding expressions that depend on negative energy eigenstates will reduce computational costs significantly. Note that if one invokes the no-pair approximation and projects on the positive-energy states, as for example in the current relativistic ADC(2) implementations,^{39,40} one would be forced to always employ approximate expressions for the diamagnetic

contributions.

Moreover, the restricted kinetic balance condition for the small component basis functions should be extended for magnetic properties to the magnetic balance condition^{50,52}, reflecting that the canonical momentum operator is extended by the vector potential in the case of magnetic interactions. In some cases one can alternatively employ unrestricted kinetically balanced basis sets, although this might lead to problems with linear dependencies⁵⁰.

2 Derivation of the SOPPA matrix elements in a non-canonical spinor basis

The equations defining SOPPA in the non-relativistic framework⁵ are well known and explicit expressions for them in terms of real canonical spatial orbitals can be found in many works^{5,42,44,53,54}. Although the starting point for the SOPPA equations is basically the same in the relativistic framework, the final non-relativistic equations cannot be applied to the relativistic case for several reasons. First of all, spin-symmetry was utilized from the start in the derivation of the non-relativistic equations, which means that the final equations were always presented in a spatial orbital basis. In the relativistic case, however, spin-symmetry no longer exists and the equations must therefore be derived in a spinor basis. Secondly, the matrix elements are always real-valued in the non-relativistic case, which was heavily exploited in the derivation of the corresponding SOPPA equations. In contrast, the matrix elements can become complex-valued in the relativistic scheme. Finally, the non-relativistic SOPPA equations are expressed in terms of canonical orbitals, which turns out to be inconvenient if one wants to analyse, e.g., magnetic properties in terms of localized orbitals⁵⁵.

This work provides the first presentation of the SOPPA equations in their most general form, i.e., in a non-canonical spin-orbital basis with explicit notation of complex conjugation. These equations can be used for a relativistic implementation of SOPPA. In addition, they represent the most general version of the non-relativistic SOPPA equations, from which

one can derive both the well known expressions in a canonical spatial orbital basis as well as new SOPPA equations in a non-canonical spatial orbital basis or in the canonical spin-orbital basis. Hence, a derivation of the equations in a spin-orbital basis with explicit notation of complex conjugation can be used to solve relativistic as well as non-relativistic problems.

In the following section the derivation of the SOPPA equations in the above mentioned form will be shown for both the matrix elements of the molecular Hessian and overlap matrix and the elements of the property gradient vectors. These equations will be normalized where appropriate and finally relations between MP-amplitudes and second order corrections to the density matrix will be utilized in order to reduce the expressions.

2.1 Matrix elements

The matrix elements of the molecular Hessian matrix, \mathbf{E} , and the overlap matrix, \mathbf{S} , defined in Eqs. (11)–(16) for SOPPA can be determined by utilizing second quantization and the following form of the operators and the second-order MP-wavefunction⁵⁶

$$\hat{H}_0 = \hat{F} + \hat{V} \quad (24)$$

$$\hat{F} = \sum_{pq} f_{pq} \hat{a}_p^\dagger \hat{a}_q = \sum_{pq} \langle p | \hat{f} | q \rangle \hat{a}_p^\dagger \hat{a}_q \quad (25)$$

$$\hat{V} = \frac{1}{2} \sum_{pqrs} g_{pqrs} \hat{a}_p^\dagger \hat{a}_r^\dagger \hat{a}_s \hat{a}_q = \frac{1}{2} \sum_{pqrs} (pq|rs) \hat{a}_p^\dagger \hat{a}_r^\dagger \hat{a}_s \hat{a}_q \quad (26)$$

$$|\Psi^{\text{MP2}}\rangle = |0\rangle + |\text{MP1}\rangle + |\text{MP2}\rangle \quad (27)$$

$$|\text{MP1}\rangle = \frac{1}{4} \sum_{cdkl} \hat{a}_c^\dagger \hat{a}_k \hat{a}_d^\dagger \hat{a}_l |0\rangle t_{kl}^{cd} \quad (28)$$

$$|\text{MP2}\rangle = \sum_{ck} \hat{a}_c^\dagger \hat{a}_k |0\rangle t_k^c + \dots \quad (29)$$

where the Hartree-Fock ground state wavefunction is denoted as $|0\rangle$. $|\Psi^{\text{MP}n}\rangle$ refers to the n 'th-order Møller-Plesset wavefunction, while $|\text{MP}n\rangle$ refers to the n 'th-order correction to the Møller-Plesset wavefunction, t_{kl}^{cd} is a MP1 double excitation amplitude, t_k^c is a MP2 single excitation amplitude. The matrix elements of the one-electron Fock operator \hat{f} in the spin-

orbital basis are $f_{pq} = \langle p | \hat{f} | q \rangle$ and $(pq|rs)$ is a two electron integral of the appropriate two-electron interaction operator, \hat{V} , in Mulliken notation. Note that only the single excitation contribution to the second-order correction to the MP-wavefunction is explicitly shown, as the remaining contributions do not lead to non-zero contributions to the SOPPA equations. Using the above relations, the matrix elements in Eqs. (11)–(20) can be evaluated to the required order. The $\mathbf{A}^{(0,1,2)}$ matrix can now be written as

$$\begin{aligned} A_{ai,bj}^{(0,1,2)} &= \langle \Psi^{\text{MP1}} | [\hat{q}_{ai}, [\hat{H}_0, \hat{q}_{bj}^\dagger]] | \Psi^{\text{MP1}} \rangle^{(0,1,2)} - \underbrace{\langle \Psi^{\text{MP1}} | [\hat{q}_{ai}, [\hat{H}_0, \hat{q}_{bj}^\dagger]] | \Psi^{\text{MP1}} \rangle^{(0)} \frac{1}{4} \sum_{cdkl} t_{kl}^{cd} t_{kl}^{cd*}}_{\text{re-normalization}} \\ &= \langle 0 | [\hat{q}_{ai}, [\hat{F}, \hat{q}_{bj}^\dagger]] | 0 \rangle + \langle 0 | [\hat{q}_{ai}, [\hat{V}, \hat{q}_{bj}^\dagger]] | 0 \rangle \\ &\quad + \langle 0 | [\hat{q}_{ai}, [\hat{V}, \hat{q}_{bj}^\dagger]] | \text{MP1} \rangle + \langle \text{MP1} | [\hat{q}_{ai}, [\hat{F}, \hat{q}_{bj}^\dagger]] | \text{MP1} \rangle \\ &\quad - \underbrace{\frac{1}{4} \langle 0 | [\hat{q}_{ai}, [\hat{F}, \hat{q}_{bj}^\dagger]] | 0 \rangle \sum_{cdkl} t_{kl}^{cd} t_{kl}^{cd*}}_{\text{re-normalization}} \end{aligned} \quad (30)$$

where only the terms up to second order, which are non-zero, have been written out explicitly.

Observe, since the MP1- and MP2-wavefunctions given by Eqs. (27)–(29) are not normalized, it is necessary to add the effect of re-normalization to second order according to

$$\begin{aligned} \mathbf{M}_N^{(0,1,2)} &= \frac{\mathbf{M}^{(0,1,2)}}{\langle 0 | 0 \rangle + \langle \text{MP1} | \text{MP1} \rangle} \approx \mathbf{M}^{(0,1,2)} \left(1 - \sum_{cdkl} \frac{1}{4} t_{kl}^{cd} t_{kl}^{cd*} \right) \\ &\Downarrow \\ \mathbf{M}_N^{(0,1,2)} &= \mathbf{M}^{(0,1,2)} - \underbrace{\mathbf{M}^{(0)} \sum_{cdkl} \frac{1}{4} t_{kl}^{cd} t_{kl}^{cd*}}_{\text{2nd-order}} \end{aligned} \quad (31)$$

Since the norm of the first-order correction to the MP1-wavefunction is already of second order, only matrix elements (and later also elements of the property gradient vectors) with a zeroth-order contribution need a correction term, and only if they have non-zero terms from the MP1- or MP2-wavefunction. Hence, only the elements of the $\mathbf{A}^{(0,1,2)}$ and $\mathbf{\Sigma}^{(0,2)}$ matrices and later the elements of the single excitation part of the property gradient vectors need

re-normalization.

By insertion of Eqs. (25)–(29) into Eq. (30) and by evaluation of the integrals in second quantization, the following re-normalized expression is obtained

$$\begin{aligned}
 A_{ai,bj}^{(0,1,2)} &= \sum_{pq}^{\text{all}} \langle 0 | [\hat{a}_i^\dagger \hat{a}_a, [\hat{a}_p^\dagger \hat{a}_q, \hat{a}_b^\dagger \hat{a}_j]] | 0 \rangle f_{pq} + \frac{1}{2} \sum_{pqrs}^{\text{all}} \langle 0 | [\hat{a}_i^\dagger \hat{a}_a, [\hat{a}_p^\dagger \hat{a}_r^\dagger \hat{a}_s \hat{a}_q, \hat{a}_b^\dagger \hat{a}_j]] | 0 \rangle g_{pqrs} \\
 &+ \frac{1}{8} \sum_{cd}^{\text{virt}} \sum_{kl}^{\text{occ}} \sum_{pqrs}^{\text{all}} \langle 0 | [\hat{a}_i^\dagger \hat{a}_a [\hat{a}_p^\dagger \hat{a}_r^\dagger \hat{a}_s \hat{a}_q, \hat{a}_b^\dagger \hat{a}_j]] \hat{a}_c^\dagger \hat{a}_k \hat{a}_d^\dagger \hat{a}_l | 0 \rangle t_{kl}^{cd} g_{pqrs} \\
 &+ \frac{1}{16} \sum_{cdef}^{\text{virt}} \sum_{klmn}^{\text{occ}} \sum_{pqrs}^{\text{all}} \langle 0 | \hat{a}_k^\dagger \hat{a}_c \hat{a}_l^\dagger \hat{a}_d [\hat{a}_i^\dagger \hat{a}_a, [\hat{a}_p^\dagger \hat{a}_q, \hat{a}_b^\dagger \hat{a}_j]] \hat{a}_e^\dagger \hat{a}_m \hat{a}_f^\dagger \hat{a}_n | 0 \rangle t_{kl}^{cd*} t_{mn}^{ef} f_{pq} \\
 &- \frac{1}{4} \sum_{pq}^{\text{all}} \sum_{cd}^{\text{virt}} \sum_{kl}^{\text{occ}} \langle 0 | [\hat{a}_i^\dagger \hat{a}_a, [\hat{a}_p^\dagger \hat{a}_q, \hat{a}_b^\dagger \hat{a}_j]] | 0 \rangle f_{pq} t_{kl}^{cd} t_{kl}^{cd*} \\
 &= \underbrace{f_{ab} \delta_{ij} - f_{ji} \delta_{ab}}_{\text{0th-order}} + \underbrace{(ai | jb) - (ab | ji)}_{\text{1st-order}} \\
 &+ \delta_{ab} \sum_{cdk} (kd | jc) t_{ik}^{dc} + \delta_{ij} \sum_{ckl} (lb | kc) t_{kl}^{ac} \\
 &+ \frac{1}{2} \delta_{ab} \sum_{cdkl} t_{kl}^{cd*} t_{il}^{cd} f_{jk} + \frac{1}{2} \delta_{ij} \sum_{cdkl} t_{kl}^{cd*} t_{kl}^{da} f_{cb} \\
 &+ \underbrace{\frac{1}{2} \sum_{ckl} t_{kl}^{bc*} t_{kl}^{ac} f_{ji} + \frac{1}{2} \sum_{cdk} t_{kj}^{cd*} t_{ik}^{cd} f_{ab}}_{\text{2nd-order}}
 \end{aligned} \tag{32}$$

Likewise, the remaining matrix elements of the Hessian and overlap matrices can be evaluated, which yields

$$\begin{aligned}
 B_{ai,bj}^{(1,2)} &= \langle \Psi^{\text{MP1}} | [\hat{a}_i^\dagger \hat{a}_a, [\hat{H}_0, \hat{a}_j^\dagger \hat{a}_b]] | \Psi^{\text{MP1}} \rangle^{(0,1,2)} \\
 &= \underbrace{(aj | bi) - (ai | bj)}_{\text{1st-order}} \\
 &+ \sum_{ck} (ki | bc) t_{jk}^{ca} + \sum_{kl} (ki | lj) t_{kl}^{ba} \\
 &+ \sum_{cd} (ad | bc) t_{ij}^{cd} + \sum_{ck} (kc | bi) t_{jk}^{ac} \\
 &+ \underbrace{\sum_{ck} (ac | kj) t_{ki}^{bc} + \sum_{ck} (kc | aj) t_{ik}^{bc}}_{\text{2nd-order}}
 \end{aligned} \tag{33}$$

$$\begin{aligned}
 C_{aibj,ck}^{(1)} &= \langle \Psi^{\text{MP1}} | [\hat{a}_i^\dagger \hat{a}_a \hat{a}_j^\dagger \hat{a}_b, [\hat{H}_0, \hat{a}_c^\dagger \hat{a}_k]] | \Psi^{\text{MP1}} \rangle^{(0,1)} \\
 &= \delta_{bc} [(aj | ki) - (ai | kj)] + \delta_{ac} [(bi | kj) - (bj | ki)] \\
 &\quad + \delta_{ik} [(bj | ac) - (bc | aj)] + \delta_{jk} [(bc | ai) - (bi | ac)]
 \end{aligned} \tag{34}$$

$$\begin{aligned}
 \tilde{C}_{ck,aibj}^{(1)} &= \langle \Psi^{\text{MP1}} | [\hat{a}_k^\dagger \hat{a}_c, [\hat{H}_0, \hat{a}_a^\dagger \hat{a}_i \hat{a}_b^\dagger \hat{a}_j]] | \Psi^{\text{MP1}} \rangle^{(0,1)} \\
 &= \delta_{bc} [(ja | ik) - (ia | jk)] + \delta_{ac} [(ib | jk) - (jb | ik)] \\
 &\quad + \delta_{ik} [(jb | ca) - (cb | ja)] + \delta_{jk} [(cb | ia) - (ib | ca)]
 \end{aligned} \tag{35}$$

$$\begin{aligned}
 D_{aibj,ckdl}^{(0)} &= \langle \Psi^{\text{MP1}} | [\hat{a}_i^\dagger \hat{a}_a \hat{a}_j^\dagger \hat{a}_b, [\hat{H}_0, \hat{a}_c^\dagger \hat{a}_k \hat{a}_d^\dagger \hat{a}_l]] | \Psi^{\text{MP1}} \rangle^{(0)} \\
 &= f_{ac} \delta_{bd} (\delta_{ik} \delta_{jl} - \delta_{il} \delta_{jk}) + f_{bc} \delta_{ad} (\delta_{il} \delta_{jk} - \delta_{ik} \delta_{jl}) \\
 &\quad + f_{ad} \delta_{bc} (\delta_{il} \delta_{jk} - \delta_{ik} \delta_{jl}) + f_{bd} \delta_{ac} (\delta_{ik} \delta_{jl} - \delta_{il} \delta_{jk}) \\
 &\quad + f_{li} \delta_{jk} (\delta_{ac} \delta_{bd} - \delta_{bc} \delta_{ad}) + f_{lj} \delta_{ik} (\delta_{bc} \delta_{ad} - \delta_{ac} \delta_{bd}) \\
 &\quad + f_{ki} \delta_{jl} (\delta_{bc} \delta_{ad} - \delta_{ac} \delta_{bd}) + f_{kj} \delta_{il} (\delta_{ac} \delta_{bd} - \delta_{bc} \delta_{ad})
 \end{aligned} \tag{36}$$

$$\begin{aligned}
 \Sigma_{ai,bj}^{(0,2)} &= \langle \Psi^{\text{MP1}} | [\hat{a}_i^\dagger \hat{a}_a, \hat{a}_b^\dagger \hat{a}_j] | \Psi^{\text{MP1}} \rangle^{(0,1,2)} \\
 &\quad - \underbrace{\frac{1}{4} \sum_{cd}^{\text{virt}} \sum_{kl}^{\text{occ}} \langle \Psi^{\text{MP1}} | [\hat{a}_i^\dagger \hat{a}_a, \hat{a}_b^\dagger \hat{a}_j] | \Psi^{\text{MP1}} \rangle^{(0)} t_{kl}^{cd*} t_{kl}^{cd}}_{\text{re-normalization}} \\
 &= \underbrace{\delta_{ij} \delta_{ab}}_{\text{0th-order}} + \underbrace{\frac{1}{2} \sum_{ckl} t_{kl}^{cb*} t_{kl}^{ac} \delta_{ij} + \frac{1}{2} \sum_{cdk} t_{jk}^{cd*} t_{ki}^{cd} \delta_{ab}}_{\text{2nd-order}}
 \end{aligned} \tag{37}$$

2.2 Property gradients

Just as for the matrix elements of the **E** and **S** matrices, the elements of the property gradients must be evaluated through second order. Here, the MP2 single excitation amplitudes, t_k^c , will be needed as well as the definitions of the property operators, \hat{P} and \hat{O} , as sums over

one electron operators, e.g., $\hat{P} = \sum_i^{N_{\text{elec}}} \hat{p}(i)$, in order to obtain the following,

$$\begin{aligned}
 {}^eT(\hat{P})_{ai}^{(0,2)} &= \langle \Psi^{\text{MP2}} | [\hat{P}, \hat{q}_{ai}^\dagger] | \Psi^{\text{MP2}} \rangle^{(0,2)} - \underbrace{\frac{1}{4} \sum_{cd}^{\text{virt}} \sum_{kl}^{\text{occ}} \langle \Psi^{\text{MP2}} | [\hat{P}, \hat{q}_{ai}^\dagger] | \Psi^{\text{MP2}} \rangle^{(0)} t_{kl}^{cd*} t_{kl}^{cd}}_{\text{re-normalization}} \\
 &= \langle 0 | [\hat{P}, \hat{q}_{ai}^\dagger] | 0 \rangle + \langle \text{MP1} | [\hat{P}, \hat{q}_{ai}^\dagger] | \text{MP1} \rangle \\
 &\quad + \langle \text{MP2} | [\hat{P}, \hat{q}_{ai}^\dagger] | 0 \rangle + \langle 0 | [\hat{P}, \hat{q}_{ai}^\dagger] | \text{MP2} \rangle \\
 &\quad - \underbrace{\frac{1}{4} \sum_{cd}^{\text{virt}} \sum_{kl}^{\text{occ}} \langle 0 | [\hat{P}, \hat{q}_{ai}^\dagger] | 0 \rangle t_{kl}^{cd*} t_{kl}^{cd}}_{\text{re-normalization}} \\
 &= \underbrace{\langle i | \hat{p} | a \rangle}_{\text{0th-order}} \\
 &\quad - \frac{1}{2} \sum_{cdkl} t_{ki}^{cd*} t_{kl}^{cd} \langle l | \hat{p} | a \rangle - \frac{1}{2} \sum_{cdkl} t_{kl}^{ad*} t_{kl}^{cd} \langle i | \hat{p} | c \rangle \\
 &\quad + \underbrace{\sum_{ck} \langle c | \hat{p} | a \rangle t_i^c - \sum_{ck} \langle i | \hat{p} | k \rangle t_k^a}_{\text{2nd-order}}
 \end{aligned} \tag{38}$$

$$\begin{aligned}
 {}^eT(\hat{O})_{ai}^{(0,2)} &= \langle \Psi^{\text{MP2}} | [\hat{q}_{ai}, \hat{O}] | \Psi^{\text{MP2}} \rangle^{(0,2)} - \underbrace{\frac{1}{4} \sum_{cd}^{\text{virt}} \sum_{kl}^{\text{occ}} \langle \Psi^{\text{MP2}} | [\hat{q}_{ai}, \hat{O}] | \Psi^{\text{MP2}} \rangle^{(0)} t_{kl}^{cd*} t_{kl}^{cd}}_{\text{re-normalization}} \\
 &= \underbrace{\langle a | \hat{o} | i \rangle}_{\text{0th-order}} \\
 &\quad - \frac{1}{2} \sum_{cdkl} t_{kl}^{cd*} t_{ki}^{cd} \langle a | \hat{o} | l \rangle - \frac{1}{2} \sum_{cdkl} t_{kl}^{cd*} t_{kl}^{ad} \langle c | \hat{o} | i \rangle \\
 &\quad + \underbrace{\sum_c \langle a | \hat{o} | c \rangle t_i^c - \sum_k \langle k | \hat{o} | i \rangle t_k^a}_{\text{2nd-order}}
 \end{aligned} \tag{39}$$

For the double excitation part of the property gradients, the elements need to be evaluated through first order⁴² only. Thus, solely the MP1-wavefunction is required.

$$\begin{aligned} {}^{\text{ee}}T(\hat{P})_{aibj}^{(1)} &= \langle \Psi^{\text{MP1}} | [\hat{P}, \hat{q}_{ai}^\dagger \hat{q}_{bj}^\dagger] | \Psi^{\text{MP1}} \rangle^{(1)} \\ &= \frac{1}{4} \sum_c \left(t_{ji}^{bc*} \langle c | \hat{p} | a \rangle - t_{ji}^{ac*} \langle c | \hat{p} | b \rangle \right) - \frac{1}{4} \sum_k \left(t_{ki}^{ab*} \langle j | \hat{p} | k \rangle - t_{kj}^{ab*} \langle i | \hat{p} | k \rangle \right) \end{aligned} \quad (40)$$

$$\begin{aligned} {}^{\text{ee}}T(\hat{O})_{aibj}^{(1)} &= \langle \Psi^{\text{MP1}} | [\hat{q}_{ai} \hat{q}_{bj}, \hat{O}] | \Psi^{\text{MP1}} \rangle^{(1)} \\ &= \frac{1}{4} \sum_c \left(t_{ji}^{bc} \langle a | \hat{o} | c \rangle - t_{ji}^{ac} \langle b | \hat{o} | c \rangle \right) - \frac{1}{4} \sum_k \left(t_{ki}^{ab} \langle k | \hat{o} | j \rangle - t_{kj}^{ab} \langle k | \hat{o} | i \rangle \right) \end{aligned} \quad (41)$$

2.3 Equations using second-order contributions to the density matrix

Finally by using the following relations, which can all be derived from expressions given by e.g., Packer et al.⁵³,

$$\rho_{ij}^{(2)} = - \sum_{cdk} \frac{1}{2} t_{jk}^{cd*} t_{ik}^{cd} \quad (42)$$

$$\rho_{ab}^{(2)} = \sum_{ckl} \frac{1}{2} t_{kl}^{ac*} t_{kl}^{bc} \quad (43)$$

$$\rho_{ai}^{(2)} = t_i^{a*} \quad (44)$$

$$\rho_{ia}^{(2)} = t_i^a \quad (45)$$

the expressions for the matrix elements can be reduced to,

$$A_{ai,bj}^{(0,1,2)} = \underbrace{f_{ab}\delta_{ij} - f_{ji}\delta_{ab}}_{\text{0th-order}} + \underbrace{(ai | jb) - (ab | ji)}_{\text{1st-order}} + \delta_{ab} \sum_{cdk} (kd | jc) t_{ik}^{dc} + \delta_{ij} \sum_{ckl} (lb | kc) t_{kl}^{ac} - \delta_{ab} \sum_l \rho_{il}^{(2)} f_{jl} - \delta_{ij} \sum_c \rho_{ca}^{(2)} f_{cb} + \underbrace{\rho_{ba}^{(2)} f_{ji} + \rho_{ij}^{(2)} f_{ab}}_{\text{2nd-order}} \quad (46)$$

$$\Sigma_{ai,bj}^{(0,2)} = \underbrace{\delta_{ij}\delta_{ab}}_{\text{0th-order}} - \underbrace{\rho_{ba}^{(2)}\delta_{ij} + \rho_{ij}^{(2)}\delta_{ab}}_{\text{2nd-order}} \quad (47)$$

$$\begin{aligned} {}^eT(\hat{P})_{ai}^{(0,2)} &= \langle i | \hat{p} | a \rangle \\ &+ \sum_l \rho_{li}^{(2)} \langle l | \hat{p} | a \rangle - \sum_c \rho_{ac}^{(2)} \langle i | \hat{p} | c \rangle \\ &+ \sum_c \rho_{ci}^{(2)} \langle c | \hat{p} | a \rangle - \sum_k \rho_{ak}^{(2)} \langle i | \hat{p} | k \rangle \\ &= \langle i | \hat{p} | a \rangle \\ &+ \sum_c \left(\rho_{ci}^{(2)} \langle c | \hat{p} | a \rangle - \rho_{ac}^{(2)} \langle i | \hat{p} | c \rangle \right) \\ &+ \sum_l \left(\rho_{li}^{(2)} \langle l | \hat{p} | a \rangle - \rho_{al}^{(2)} \langle i | \hat{p} | l \rangle \right) \end{aligned} \quad (48)$$

$$\begin{aligned} {}^eT(\hat{O})_{ai}^{(0,2)} &= \langle a | \hat{o} | i \rangle \\ &+ \sum_l \rho_{il}^{(2)} \langle a | \hat{o} | l \rangle - \sum_c \rho_{ca}^{(2)} \langle c | \hat{o} | i \rangle \\ &+ \sum_c \rho_{ic}^{(2)} \langle a | \hat{o} | c \rangle - \sum_k \rho_{ka}^{(2)} \langle k | \hat{o} | i \rangle \\ &= \langle a | \hat{o} | i \rangle \\ &+ \sum_c \left(\rho_{ic}^{(2)} \langle a | \hat{o} | c \rangle - \rho_{ca}^{(2)} \langle c | \hat{o} | i \rangle \right) \\ &+ \sum_l \left(\rho_{il}^{(2)} \langle a | \hat{o} | l \rangle - \rho_{la}^{(2)} \langle l | \hat{o} | i \rangle \right) \end{aligned} \quad (49)$$

Note that the elements of the remaining matrices as well as the remaining elements of the property gradient vectors given in Eqs. (40) and (41) cannot be further reduced using the

above relations between the amplitudes and the second-order corrections to the density matrix and hence these will not be repeated here.

3 Reduction of computational costs

Clearly, it is desirable to perform the calculation as fast and using as little memory as possible. Different ways of achieving this objective within a relativistic framework are discussed in the following sections, including the use of relativistic symmetries and solving the equations in a reduced vector space.

3.1 Kramers Pairs

A convenient way of saving computer resources is utilizing Kramers Pairs. In relativistic quantum chemistry spin-symmetry is broken due to spin-orbit coupling. Instead, it is replaced by time-reversal symmetry in the absence of external magnetic fields and in the case where the external field is considered as a perturbation⁴⁷. It was introduced by Kramers in 1930⁵⁷, where he proved that each fermionic state is doubly degenerate, i.e., fermions come in Kramers pairs⁴⁶. The spinors of two such fermions are related through the Kramers time-reversal symmetry operator $\hat{\mathcal{K}}$,

$$\hat{\mathcal{K}}|\psi_p\rangle = |\psi_{\bar{p}}\rangle \quad \text{and} \quad \hat{\mathcal{K}}|\psi_{\bar{p}}\rangle = -|\psi_p\rangle \quad (50)$$

$$\Downarrow$$

$$\hat{\mathcal{K}}^2|\psi_p\rangle = -|\psi_p\rangle \quad (51)$$

where the time-reversal operator is defined as

$$\hat{\mathcal{K}} = -i \begin{pmatrix} \sigma_y & 0 \\ 0 & \sigma_y \end{pmatrix} \hat{\mathcal{K}}_0 \quad (52)$$

and $\hat{\mathcal{K}}_0$ performs complex conjugation. Thus, if the time-reversal symmetry operator, $\hat{\mathcal{K}}$, works on a scalar, the effect is simply complex conjugation. Hence, for a matrix element Ω_{pq}

$$\hat{\mathcal{K}}\Omega_{pq} = \hat{\mathcal{K}}\langle p | \hat{\Omega} | q \rangle = \langle \bar{p} | \hat{\hat{\Omega}} | \bar{q} \rangle = t\langle \bar{p} | \hat{\Omega} | \bar{q} \rangle = t\Omega_{\bar{p}\bar{q}} \quad (53)$$

where $|q\rangle = |\psi_q\rangle$ and $t = 1$ if $\hat{\Omega}$ is symmetric with respect to time-reversal symmetry and $t = -1$ if it is antisymmetric. As Ω_{pq} is a scalar, we also know that

$$\hat{\mathcal{K}}\Omega_{pq} = \Omega_{pq}^* \quad (54)$$

Likewise,

$$\hat{\mathcal{K}}\Omega_{\bar{p}\bar{q}} = \mathcal{K}\langle \bar{p} | \hat{\Omega} | \bar{q} \rangle = -\langle p | \hat{\hat{\Omega}} | q \rangle = -t\langle p | \hat{\Omega} | q \rangle = -t\Omega_{pq} \quad (55)$$

In general, if the time-reversal symmetry, t , of the operator, Ω , is known and a Kramers paired basis is used, the matrix representation of the operator $\hat{\Omega}$ can be written in the simplified block structure of Eq. (56) by utilizing Eqs. (53)–(55).

$$\begin{pmatrix} \Omega_{pq} & \Omega_{p\bar{q}} \\ \Omega_{\bar{p}q} & \Omega_{\bar{p}\bar{q}} \end{pmatrix} \rightarrow \begin{pmatrix} \mathbf{X} & \mathbf{Y} \\ -t\mathbf{Y}^* & t\mathbf{X}^* \end{pmatrix} \quad (56)$$

In the above matrix, spinors are ordered with all indices p first, *then* followed by all Kramers partners, indices \bar{p} . Each block of the matrix is denoted as $\mathbf{\Omega}_{pq}$ containing all elements Ω_{pq} . In addition,

$$X_{pq} = \langle p | \hat{\Omega} | q \rangle = \Omega_{pq} = t\Omega_{\bar{p}\bar{q}}^* = tX_{\bar{p}\bar{q}}^* \quad (57)$$

$$Y_{pq} = \langle p | \hat{\Omega} | \bar{q} \rangle = \Omega_{p\bar{q}} = -t\Omega_{\bar{p}q}^* = -tY_{\bar{p}q}^* \quad (58)$$

Thus, the number of unique matrix elements is reduced by a factor of two, as the elements of the upper segment are connected to those of the lower segment.

The above can obviously be applied to the elements of the property gradients, but it can likewise be used to connect the matrix elements of the Hessian and overlap matrices, e.g., $A_{ai,bj}^{(0,1,2)} = A_{\bar{a}i,\bar{b}j}^{(0,1,2)*}$.

3.2 Hermiticity

Following the implementation by Saue and Jensen for RPA⁵⁶ to further reduce the demands on computational resources, we can consider the hermiticity of an operator (this is also exploited in the non-relativistic framework)

$$\Omega_{pq}^* = \langle p | \hat{\Omega} | q \rangle^* = \langle q | \hat{\Omega}^* | p \rangle = h \langle q | \hat{\Omega} | p \rangle = h \Omega_{qp} \quad (59)$$

where $h = 1$ for a hermitian operator and $h = -1$ for an antihermitian operator. We can now write

$$\Omega_{pq} = t \Omega_{\bar{p}\bar{q}}^* = h \Omega_{qp}^* = th \Omega_{\bar{q}\bar{p}} \quad (60)$$

and it is clear that the number of unique matrix elements has been reduced by a factor of four. Note that, as we usually order all vectors as well as matrices in blocks of excitations and de-excitations, the above relation from hermiticity connects the excitation and de-excitation segments, whereas the time-reversal symmetry connects elements within each of the (de-)excitation blocks shown in Eq. (56).

A vector consisting of an excitation and a de-excitation part now takes the form

$$\mathbf{U}_1(h_1, t_1) = \begin{pmatrix} V(t_1) \\ h_1 V(t_1)^* \end{pmatrix} \quad (61)$$

The product of two such vectors can be split into three cases:⁵⁶

- If $h_1 h_2 = -t_1 t_2$, the product is zero.
- If $h_1 h_2 = t_1 t_2 = 1$, the product is real.
- If $h_1 h_2 = t_1 t_2 = -1$, the product is imaginary.

In general, property operators are hermitian and so the form of the property gradient vector simplifies to

$$\mathbf{T}(\hat{O})(t) = \begin{pmatrix} g(t) \\ g(t)^* \end{pmatrix} \quad (62)$$

3.3 Quaternion algebra

A practical way of realizing the reduced dimension of the problem at hand is utilizing quaternion algebra (the same reductions have also been obtained in an alternative way by, e.g., Visscher⁵⁸). Quaternion algebra is defined similarly to complex algebra. Like a complex number, a quaternion number, Q , can be defined as having four rather than two components in the following way:

$$Q = a + \check{i}b + \check{j}c + \check{k}d \quad (63)$$

where a , b , c , and d are real numbers, whereas \check{i} , \check{j} , and \check{k} are all imaginary phases. An advantage of quaternion compared to complex algebra is that no imaginary component is singled out, corresponding to choosing a particular axis such as the z -axis along which the spin is quantized.⁵⁹ In quaternion algebra all imaginary phases are equivalent and can be cyclically permuted. Thus, the imaginary phase in a complex number can be identified as any of the imaginary phases of the quaternion number. Finally, the three imaginary phases in quaternion algebra can be identified as the complex imaginary phase multiplied with one

of the Pauli spin matrices⁵⁹

$$\check{i} \rightarrow i\sigma_z \quad (64)$$

$$\check{j} \rightarrow i\sigma_y \quad (65)$$

$$\check{k} \rightarrow i\sigma_x \quad (66)$$

All integrals over complex orbitals can be written in quaternion form using Kramers partners⁶⁰,

$$\begin{aligned} Q(pq) | &= (\Re(pq) | + (\Im(pq) | \check{i} + (\Re(p\bar{q}) | \check{j} + (\Im(p\bar{q}) | \check{k}) \quad (67) \\ Q(pq | rs) &= [(\Re(pq) | + (\Im(pq) | \check{i} + (\Re(p\bar{q}) | \check{j} + (\Im(p\bar{q}) | \check{k})] \\ &\times [(\Re(rs) | + (\Im(rs) | \check{i} + (\Re(r\bar{s}) | \check{j} + (\Im(r\bar{s}) | \check{k})] \\ &= [(\Re(pq) | \Re(rs)) - (\Im(pq) | \Im(rs)) - (\Re(p\bar{q}) | \Re(r\bar{s})) - (\Im(p\bar{q}) | \Im(r\bar{s}))] \\ &+ [(\Re(pq) | \Im(rs)) + (\Im(pq) | \Re(rs)) + (\Re(p\bar{q}) | \Im(r\bar{s})) - (\Im(p\bar{q}) | \Re(r\bar{s}))] \check{i} \\ &+ [(\Re(pq) | \Re(r\bar{s})) + (\Im(pq) | \Im(r\bar{s})) + (\Re(p\bar{q}) | \Re(rs)) - (\Im(p\bar{q}) | \Im(rs))] \check{j} \\ &+ [(\Re(pq) | \Im(r\bar{s})) + (\Im(pq) | \Re(r\bar{s})) - (\Re(p\bar{q}) | \Im(rs)) + (\Im(p\bar{q}) | \Re(rs))] \check{k} \quad (68) \end{aligned}$$

In the above, the superscript Q signifies that the number is in quaternion form and $\Re(pq)$ and $\Im(pq)$ are the real and imaginary parts of a charge distribution in orbitals p and q , respectively. One electron integrals are integrals over one charge distribution and can therefore be written in quaternion form equivalent to Eq. (67), while two-electron integrals as shown in Eq. (68) are integrals over two charge distributions and can be written in the quaternion form given above. So far, the integrals are just reordered compared to a complex form, but the quaternion form can now be used to reduce the number of needed integrals *if* symmetry is also considered.

In non-relativistic chemistry symmetry is described by utilizing (single) point groups,

but as these do not include spin, they are generally not sufficient in relativistic quantum chemistry. An additional symmetry operation must be added, as the identity operation now refers to a 4π rotation. A 2π rotation results in a change of sign for fermions, while it leaves bosonic wavefunctions unchanged.⁴⁷ Point groups including this new identity are referred to as double groups, since they can be found as direct products of the single point groups and a group consisting of the 4π and 2π rotations. Note that the irreducible representations (irreps) that describe bosons are equivalent to the single point group irreps.

Systems that contain an even number of fermions can be approximated as bosonic, which can reduce the number of matrices that need to be stored. A (single) point group, for example, that contains several rotation axes or mirror planes, e.g., C_{2v} , will have many distinguishable ways of rotating the orbitals due to many irreps and hence there are no equivalent axes, which then reduces the quaternion problem to a real one. Thus, it is only necessary to store the first four of the sixteen integral contributions presented in Eq. (68)⁶¹ as opposed to eight in the complex case (here the third line of contributions in Eq. (68) would also need storing). If, however, the point group contains only one rotation axis or one mirror plane, e.g., C_s , it will have one “special” axis, which introduces the need for an imaginary component. Hence, the problem becomes complex and the first eight of the integral contributions in Eq. (68) must be stored, as opposed to all in the complex formalism. Finally, for a point group containing no rotation axis or plane, i.e., C_1 , all orbitals must transform as the same irrep and hence all orbital rotations are equivalent. Thus, three equivalent axes are needed, which means the problem cannot be reduced from quaternion form and so all sixteen contributions to the two-electron integrals must be stored. For one-electron integrals, one, two, or all four contributions must be stored for the three symmetry types, respectively, when the quaternion form is utilized.

3.4 Solving the SOPPA equations in a reduced space

3.4.1 Expansion in a set of trial vectors

In relativistic as well as non-relativistic theory, the \mathbf{E} and \mathbf{S} matrices are often too large to be explicitly calculated and stored. Neither the inhomogeneous problem in Eq. (7) nor the eigenvalue problem in Eq. (8) can be solved explicitly using these matrices. Instead, one expands the unknown solution- or eigenvector, \mathbf{X} , in a set of trial vectors, \mathbf{b}_i ,⁶²

$$\mathbf{X} = \sum_i c_i \mathbf{b}_i \quad (69)$$

with c_i being expansion coefficients.

Hence, one can rewrite the inhomogeneous set of equations,

$$(\omega \tilde{\mathbf{S}} - \tilde{\mathbf{E}})\mathbf{c} = \tilde{\mathbf{T}}(\hat{O}) \quad (70)$$

as well as the homogeneous set of equations,

$$\tilde{\mathbf{E}}\mathbf{c} = \omega \tilde{\mathbf{S}}\mathbf{c} \quad (71)$$

where in both cases only the reduced matrices need to be stored,

$$\tilde{\mathbf{E}} = \mathbf{R}^\dagger \mathbf{E} \mathbf{R} = \mathbf{R}^\dagger \boldsymbol{\sigma} \quad (72)$$

$$\tilde{\mathbf{S}} = \mathbf{R}^\dagger \mathbf{S} \mathbf{R} = \mathbf{R}^\dagger \boldsymbol{\tau} \quad (73)$$

$$\tilde{\mathbf{T}}(\hat{O}) = \mathbf{R}^\dagger \mathbf{T}(\hat{O}) \quad (74)$$

In Eqs. (72)–(74), \mathbf{R} is a matrix with the trial vectors, \mathbf{b}_i , as its columns.

In addition to the reduction in the required memory, for the most costly part, the $\mathbf{B}^{(2)}$ contribution, the cost is significantly reduced from N^6 to N^5 .⁵³

For an additional reduction of the required computational resources, it is convenient to

rewrite the trial vector in the form of Eq. (61). From Eq. (2), the solution vector can be found to take the form⁵⁶,

$$\mathbf{X}(\omega) = \begin{pmatrix} \mathbf{Z} \\ \mathbf{Y}^* \end{pmatrix} \quad (75)$$

$$\mathbf{X}(-\omega) = \begin{pmatrix} \mathbf{Y} \\ \mathbf{Z}^* \end{pmatrix} \quad (76)$$

By employing a linear combination of solution vectors for $\pm\omega$, a vector of the desired structure can be constructed. The effect of the \mathbf{E} and \mathbf{S} matrices on the solution vector and hence on the trial vectors can now be investigated. It turns out that both the \mathbf{E} and \mathbf{S} matrices conserve time-reversal symmetry, but while the \mathbf{E} matrix also conserves hermiticity, the \mathbf{S} matrix reverses it.⁵⁶ Thus, the \mathbf{E} matrix couples trial vectors of same hermiticity, while the \mathbf{S} matrix couples trial vectors of opposite hermiticity.

3.4.2 σ and τ vectors using one-index transformed matrix elements

For the implementation of either a relativistic or a completely general complex non-relativistic SOPPA, the reduced matrices in Eqs. (72) and (73) must be determined, since the full Hessian and overlap matrices are never explicitly constructed. Particularly, the σ and τ vectors, defined in Eqs. (72) and (73), are of interest, as the construction of the reduced matrices from those are trivial^{53,54,56}. As noted by Saue and Jensen⁵⁶, the RPA σ vector can be rewritten using one-index transformed integrals. The one-index transformation is a convenient way of simplifying the equations, which not only reduces the number of terms written, but also naturally splits the equations in terms that can be implemented separately, which has also been utilized previously with advantage for the SOPPA equations in the spatial orbital basis^{53,54}. The present new non-canonical equations in the spin-orbital basis will therefore also be one-index transformed and final SOPPA equations in the reduced space are obtained.

The generalized form of the σ vector is shown below. The trial vectors can be given the

form $\mathbf{b}^T = ({}^e\mathbf{b}, {}^d\mathbf{b}, {}^{ee}\mathbf{b}, {}^{dd}\mathbf{b}) = ({}^e\mathbf{b}, {}^e\mathbf{b}^*, {}^{ee}\mathbf{b}, {}^{ee}\mathbf{b}^*)$, where ${}^e\mathbf{b}$ and ${}^{ee}\mathbf{b}$ refer to the single and double excitation parts of the vector, respectively, due to the conservation of hermiticity by the Hessian⁵⁶. The trial vector matrix can then be written as $\mathbf{R}^T = ({}^e\mathbf{R}, {}^e\mathbf{R}^*, {}^{ee}\mathbf{R}, {}^{ee}\mathbf{R}^*)$. Here, it should be mentioned that the matrices ${}^e\mathbf{R}$ and ${}^{ee}\mathbf{R}$ are not (usually) quadratic. We thus get

$$\begin{pmatrix} {}^e\boldsymbol{\sigma} \\ {}^{ee}\boldsymbol{\sigma} \\ {}^d\boldsymbol{\sigma} \\ {}^{dd}\boldsymbol{\sigma} \end{pmatrix} = \begin{pmatrix} \mathbf{A}^{(0,1,2)}{}^e\mathbf{R} + \mathbf{B}^{(1,2)}{}^e\mathbf{R}^* + \tilde{\mathbf{C}}^{(1)}{}^{ee}\mathbf{R} \\ \mathbf{C}^{(1)}{}^e\mathbf{R} + \mathbf{D}^{(0)}{}^{ee}\mathbf{R} \\ \mathbf{A}^{(0,1,2)*}{}^e\mathbf{R}^* + \mathbf{B}^{(1,2)*}{}^e\mathbf{R} + \tilde{\mathbf{C}}^{(1)*}{}^{ee}\mathbf{R}^* \\ \mathbf{C}^{(1)*}{}^e\mathbf{R}^* + \mathbf{D}^{(0)*}{}^{ee}\mathbf{R}^* \end{pmatrix} = \begin{pmatrix} {}^e\boldsymbol{\sigma} \\ {}^{ee}\boldsymbol{\sigma} \\ {}^e\boldsymbol{\sigma}^* \\ {}^{ee}\boldsymbol{\sigma}^* \end{pmatrix} \quad (77)$$

Note that in order to obtain solution vectors of the form given in Eqs. (75) and (76), the blocks of the spinors and matrices and thus also the $\boldsymbol{\sigma}$ vectors have been reordered.

From the blocks of the $\boldsymbol{\sigma}$ vector in Eq. (77) it can be seen that it is necessary to evaluate only

$${}^e\boldsymbol{\sigma} = \mathbf{A}^{(0,1,2)}{}^e\mathbf{R} + \mathbf{B}^{(1,2)}{}^e\mathbf{R}^* + \tilde{\mathbf{C}}^{(1)}{}^{ee}\mathbf{R}$$

and

$${}^{ee}\boldsymbol{\sigma} = \mathbf{C}^{(1)}{}^e\mathbf{R} + \mathbf{D}^{(0)}{}^{ee}\mathbf{R}$$

Equivalently, the elements of the $\boldsymbol{\tau}$ vector can be determined, but since the overlap matrix reverses hermiticity, the $\boldsymbol{\tau}$ vector will be antihermitian rather than hermitian⁵⁶.

For the sake of readability of the equations it is now convenient to split up the expressions of the single and double excitation parts of the $\boldsymbol{\sigma}$ vector. The full single- and double excitation parts of the $\boldsymbol{\sigma}$ vector will furthermore be labelled with a ‘‘SOPPA’’ superscript.

$${}^e\boldsymbol{\sigma}^{\text{SOPPA}} = {}^e\boldsymbol{\sigma}^{\text{RPA}} + {}^e\boldsymbol{\sigma}^{\text{2nd}} + {}^e\boldsymbol{\sigma}^{\text{double}} \quad (78)$$

$${}^{ee}\boldsymbol{\sigma}^{\text{SOPPA}} = {}^{ee}\boldsymbol{\sigma}^{\text{single}} + {}^{ee}\boldsymbol{\sigma}^{\text{double}} \quad (79)$$

with

$${}^e\sigma^{\text{RPA}} = \mathbf{A}^{(0,1)}{}^e\mathbf{R} + \mathbf{B}^{(1)}{}^e\mathbf{R}^* \quad (80)$$

$${}^e\sigma^{2\text{nd}} = \mathbf{A}^{(2)}{}^e\mathbf{R} + \mathbf{B}^{(2)}{}^e\mathbf{R}^* \quad (81)$$

$${}^e\sigma^{\text{double}} = \tilde{\mathbf{C}}^{(1)}{}^{ee}\mathbf{R} \quad (82)$$

$${}^{ee}\sigma^{\text{single}} = \mathbf{C}^{(1)}{}^e\mathbf{R} \quad (83)$$

$${}^{ee}\sigma^{\text{double}} = \mathbf{D}^{(0)}{}^{ee}\mathbf{R} \quad (84)$$

Note that ${}^e\sigma^{\text{RPA}}$ is the σ vector presented for the RPA calculation⁵⁶ and ${}^e\sigma^{\text{RPA}} + {}^e\sigma^{2\text{nd}}$ is the σ vector needed for an HRPDA calculation.

The terms of the single excitation part of the σ vector can thus be written as follows,

$$\begin{aligned} {}^e\sigma_{ai}^{\text{RPA}} &= \sum_{bj} A_{ai,bj}^{(0,1)} {}^eb_{bj} + \sum_{bj} B_{ai,bj}^{(1)} {}^eb_{bj}^* \\ &= \sum_{bj} f_{ab}\delta_{ij} {}^eb_{bj} - \sum_{bj} f_{ji}\delta_{ab} {}^eb_{bj} + \sum_{bj} (ai | jb) {}^eb_{bj} - \sum_{bj} (ab | ji) {}^eb_{bj} \\ &\quad + \sum_{bj} (aj | bi) {}^eb_{jb} - \sum_{bj} (ai | bj) {}^eb_{jb} \end{aligned} \quad (85)$$

$$\begin{aligned}
 {}^e\sigma_{ai}^{2nd} &= \sum_{bj} A_{ai,bj}^{(2)} {}^e b_{bj} + \sum_{bj} B_{ai,bj}^{(2)} {}^e b_{bj}^* \\
 &= \sum_{bj} \delta_{ab} \sum_{cdk} (kd | jc) t_{ik}^{dc} {}^e b_{bj} + \sum_{bj} \delta_{ij} \sum_{ckl} (lb | kc) t_{kl}^{ac} {}^e b_{bj} \\
 &\quad + \sum_{bj} \delta_{ab} \sum_l \rho_{il} f_{jl} {}^e b_{bj} - \sum_{bj} \delta_{ij} \sum_c \rho_{ca} f_{cb} {}^e b_{bj} \\
 &\quad + \sum_{bj} \rho_{ba} f_{ji} {}^e b_{bj} + \sum_{bj} \rho_{ij} f_{ab} {}^e b_{bj} \\
 &\quad + \sum_{bj} \sum_{ck} (ki | bc) t_{jk}^{ca} {}^e b_{jb} + \sum_{bj} \sum_{kl} (ik | lj) t_{kl}^{ba} {}^e b_{jb} \\
 &\quad + \sum_{bj} \sum_{cd} (ad | bc) t_{ij}^{cd} {}^e b_{jb} + \sum_{bj} \sum_{ck} (kc | bi) t_{jk}^{ac} {}^e b_{jb} \\
 &\quad + \sum_{bj} \sum_{ck} (ac | kj) t_{ki}^{bc} {}^e b_{jb} + \sum_{bj} \sum_{ck} (kc | aj) t_{ik}^{bc} {}^e b_{jb} \\
 &= \sum_j \sum_{cdk} (kd | jc) t_{ik}^{dc} {}^e b_{aj} + \sum_b \sum_{ckl} (lb | kc) t_{kl}^{ac} {}^e b_{bi} \\
 &\quad + \sum_j \sum_l \rho_{il} f_{jk} {}^e b_{aj} - \sum_b \sum_c \rho_{ca} f_{cb} {}^e b_{bi} \\
 &\quad + \sum_{bj} \rho_{ba} f_{ji} {}^e b_{bj} + \sum_{bj} \rho_{ij} f_{ab} {}^e b_{bj} \\
 &\quad + \sum_{bj} \sum_{cd} (ad | bc) t_{ij}^{cd} {}^e b_{jb} + \sum_{bj} \sum_{ck} (kc | bi) t_{jk}^{ac} {}^e b_{jb} \\
 &\quad + \sum_{bj} \sum_{cd} (ad | bc) t_{ij}^{cd} {}^e b_{jb} + \sum_{bj} \sum_{ck} (kc | bi) t_{jk}^{ac} {}^e b_{jb} \\
 &\quad + \sum_{bj} \sum_{ck} (ac | kj) t_{ki}^{bc} {}^e b_{jb} + \sum_{bj} \sum_{ck} (kc | aj) t_{ik}^{bc} {}^e b_{jb}
 \end{aligned} \tag{86}$$

$$\begin{aligned}
 {}^e\sigma_{ai}^{double} &= \sum_{cdkl} \tilde{C}_{ai,ckdl}^{(1)} {}^{ee} b_{ckdl} \\
 &= \sum_{cdkl} \delta_{da} [(lc | ki) - (kc | li)] {}^{ee} b_{ckdl} + \sum_{cdkl} \delta_{ca} [(kd | li) - (ld | ki)] {}^{ee} b_{ckdl} \\
 &\quad + \sum_{cdkl} \delta_{ki} [(ld | ac) - (ad | lc)] {}^{ee} b_{ckdl} + \sum_{cdkl} \delta_{li} [(ad | kc) - (kd | ac)] {}^{ee} b_{ckdl} \\
 &= \sum_{ckl} [(lc | ki) - (kc | li)] [{}^{ee} b_{ckal} + {}^{ee} b_{alck}] \\
 &\quad + \sum_{cdk} [(kd | ac) - (ad | kc)] [{}^{ee} b_{cidk} + {}^{ee} b_{dkci}]
 \end{aligned} \tag{87}$$

$$\begin{aligned}
 {}^{ee}\sigma_{aibj}^{\text{single}} &= \sum_{ck} C_{aibj,ck}^{(1)} {}^eb_{ck} \\
 &= \sum_{ck} \delta_{bc} [(aj | ki) - (ai | kj)] {}^eb_{ck} + \sum_{ck} \delta_{ac} [(bi | kj) - (bj | ki)] {}^eb_{ck} \\
 &\quad + \sum_{ck} \delta_{ik} [(bj | ac) - (bc | aj)] {}^eb_{ck} + \sum_{ck} \delta_{jk} [(bc | ai) - (bi | ac)] {}^eb_{ck} \\
 &= \sum_k [(aj | ki) - (ai | kj)] {}^eb_{bk} + \sum_k [(bi | kj) - (bj | ki)] {}^eb_{ak} \\
 &\quad + \sum_c [(bj | ac) - (bc | aj)] {}^eb_{ci} + \sum_c [(bc | ai) - (bi | ac)] {}^eb_{cj} \quad (88)
 \end{aligned}$$

$$\begin{aligned}
 {}^{ee}\sigma_{aibj}^{\text{double}} &= \sum_{ckdl} D_{aibj,ckdl}^{(0)} {}^{ee}b_{ckdl} \\
 &= \sum_{ckdl} f_{ac} \delta_{bd} (\delta_{ik} \delta_{jl} - \delta_{il} \delta_{jk}) {}^{ee}b_{ckdl} + \sum_{ckdl} f_{bc} \delta_{ad} (\delta_{il} \delta_{jk} - \delta_{ik} \delta_{jl}) {}^{ee}b_{ckdl} \\
 &\quad + \sum_{ckdl} f_{ad} \delta_{bc} (\delta_{il} \delta_{jk} - \delta_{ik} \delta_{jl}) {}^{ee}b_{ckdl} + \sum_{ckdl} f_{bd} \delta_{ac} (\delta_{ik} \delta_{jl} - \delta_{il} \delta_{jk}) {}^{ee}b_{ckdl} \\
 &\quad + \sum_{ckdl} f_{li} \delta_{jk} (\delta_{ac} \delta_{bd} - \delta_{bc} \delta_{ad}) {}^{ee}b_{ckdl} + \sum_{ckdl} f_{lj} \delta_{ik} (\delta_{bc} \delta_{ad} - \delta_{ac} \delta_{bd}) {}^{ee}b_{ckdl} \\
 &\quad + \sum_{ckdl} f_{ki} \delta_{jl} (\delta_{bc} \delta_{ad} - \delta_{ac} \delta_{bd}) {}^{ee}b_{ckdl} + \sum_{ckdl} f_{kj} \delta_{il} (\delta_{ac} \delta_{bd} - \delta_{bc} \delta_{ad}) {}^{ee}b_{ckdl} \\
 &= \sum_c f_{ac} [{}^{ee}b_{cibj} - {}^{ee}b_{cjb i} + {}^{ee}b_{bjci} - {}^{ee}b_{bicj}] \\
 &\quad + \sum_c f_{bc} [{}^{ee}b_{cja i} - {}^{ee}b_{ciaj} + {}^{ee}b_{aicj} - {}^{ee}b_{ajci}] \\
 &\quad + \sum_k f_{ki} [{}^{ee}b_{ajbk} - {}^{ee}b_{bjak} + {}^{ee}b_{bkaj} - {}^{ee}b_{akbj}] \\
 &\quad + \sum_k f_{kj} [{}^{ee}b_{biak} - {}^{ee}b_{aibk} + {}^{ee}b_{akbi} - {}^{ee}b_{bkai}] \quad (89)
 \end{aligned}$$

Introducing the one-index transformed Fock matrices and two-electron integrals^{53,61},

$$\tilde{F}_{pq} = \left[\underbrace{\sum_t eb_{pt}f_{tq}}_{F_{\tilde{p}q}} - \underbrace{\sum_t eb_{tq}f_{pt}}_{F_{p\tilde{q}}} \right] \quad (90)$$

$$(\tilde{p}\tilde{q} | rs) = \left[\underbrace{\sum_o eb_{po}(oq | rs)}_{(\tilde{p}q|rs)} - \underbrace{\sum_o eb_{oq}(po | rs)}_{(p\tilde{q}|rs)} \right] \quad (91)$$

$$\tilde{g}_{pqrs} = (pq | \widetilde{rs}) = (\tilde{p}\tilde{q} | rs) + (pq | \widetilde{rs}) \quad (92)$$

$$\tilde{G}_{pq} = \sum_j \left[(pq | \widetilde{j\tilde{j}}) - \underbrace{\sum_t eb_{jt}(pj | tq)}_{(p\tilde{j}|\tilde{j}q)} + \underbrace{\sum_t eb_{tj}(pt | jq)}_{(p\tilde{j}|jq)} \right], \quad (93)$$

Eq. (85) can be rewritten as

$$\begin{aligned} {}^e\sigma_{ai}^{\text{RPA}} &= -\tilde{F}_{ai} + \sum_j (ai | \widetilde{j\tilde{j}}) - \sum_j (a\tilde{j} | j\tilde{i}) \\ &\quad + \sum_j (aj | \tilde{j}\tilde{i}) - \sum_j (ai | \tilde{j}\tilde{j}) \\ &= -\tilde{F}_{ai} - \tilde{G}_{ai} \\ &= -(\tilde{F}_{ai} + \tilde{G}_{ai}) \end{aligned} \quad (94)$$

Which is the already known RPA σ vector. Likewise, the other terms of the single excitation part of the SOPPA σ vector can be written as:

$$\begin{aligned}
 {}^e\sigma_{ai}^{2\text{nd}} = & \sum_{cdk} (kd \mid \tilde{a}c) t_{ik}^{dc} + \sum_{ckl} (\tilde{l}i \mid kc) t_{kl}^{ac} \\
 & + \sum_l \rho_{il} F_{\tilde{a}l} - \sum_c \rho_{ca} F_{c\tilde{i}} \\
 & + \sum_b \rho_{ba} F_{b\tilde{i}} + \sum_j \rho_{ij} F_{a\tilde{j}} \\
 & + \sum_j \sum_{ck} (ki \mid \tilde{j}c) t_{jk}^{ca} + \sum_b \sum_{kl} (ki \mid l\tilde{b}) t_{kl}^{ba} \\
 & + \sum_j \sum_{cd} (ad \mid \tilde{j}c) t_{ij}^{cd} + \sum_j \sum_{ck} (kc \mid \tilde{j}i) t_{jk}^{ac} \\
 & + \sum_b \sum_{ck} (ac \mid k\tilde{b}) t_{ki}^{bc} + \sum_b \sum_{ck} (kc \mid a\tilde{b}) t_{ik}^{bc}
 \end{aligned} \tag{95}$$

A reordering of terms followed by a relabelling of the summation indices yields,

$$\begin{aligned}
 {}^e\sigma_{ai}^{2\text{nd}} = & \sum_{cdk} (\tilde{a}c \mid kd) t_{ki}^{cd} - \sum_{cdk} (a\tilde{c} \mid kd) t_{ki}^{cd} \\
 & + \sum_{cdk} (ac \mid \tilde{k}d) t_{ki}^{cd} - \sum_{cdk} (ac \mid k\tilde{d}) t_{ki}^{cd} \\
 & + \sum_{ckl} (kc \mid \tilde{l}i) t_{kl}^{ac} - \sum_{ckl} (kc \mid l\tilde{i}) t_{kl}^{ac} \\
 & + \sum_{ckl} (k\tilde{c} \mid li) t_{kl}^{ac} - \sum_{ckl} (\tilde{k}c \mid li) t_{kl}^{ac} \\
 & + \sum_l \rho_{il} F_{\tilde{a}l} - \sum_l \rho_{il} F_{a\tilde{l}} \\
 & - \sum_c \rho_{ca} F_{c\tilde{i}} - \sum_c \rho_{ca} F_{c\tilde{i}} \\
 = & \sum_{cdk} \left[(\tilde{a}\tilde{c} \mid kd) + (ac \mid \tilde{k}d) \right] t_{ki}^{cd} \\
 & + \sum_{ckl} \left[(kc \mid \tilde{l}i) + (\tilde{k}c \mid li) \right] t_{kl}^{ca} \\
 & + \frac{1}{2} \sum_{cdkl} t_{kl}^{cd*} t_{il}^{cd} \tilde{F}_{ak} + \sum_c \rho_{ca} \tilde{F}_{ci} \\
 = & \sum_{cdk} \tilde{g}_{ackd} t_{ki}^{cd} + \sum_{ckl} \tilde{g}_{kcli} t_{kl}^{ca} \\
 & + \sum_l \rho_{il} \tilde{F}_{al} + \sum_c \rho_{ca} \tilde{F}_{ci}
 \end{aligned} \tag{96}$$

The remaining term of the single excitation part of the σ vector in Eq. (87) cannot be written in a one-index transformed way and will therefore not be repeated here. The double excitation part of the σ vector takes the following form when one index transformed,

$$\begin{aligned} {}^{\text{ee}}\sigma_{aibj}^{\text{single}} &= (aj | \tilde{bi}) - (ai | \tilde{bj}) + (bi | \tilde{aj}) - (bj | \tilde{ai}) \\ &\quad + (bj | \tilde{ai}) - (\tilde{bi} | aj) + (\tilde{bj} | ai) - (bi | \tilde{aj}) \\ &= \tilde{g}_{ajbi} - \tilde{g}_{aibj} \end{aligned} \quad (97)$$

The last term of the double excitation part of the σ vector in Eq. (89) cannot be expressed in one-index transformed quantities either and hence cannot be further reduced. The single excitation part of the τ vector, however, can be one-index transformed and is found to be,

$${}^{\text{e}}\tau_{ai}^{\text{SOPPA}} = b_{ai} - \sum_b \rho_{ba}^{(2)} b_{bi} + \sum_j \rho_{ij}^{(2)} b_{aj} \quad (98)$$

Eq. (98) is identical in form to the expression obtained in the non-relativistic case with only spatial orbitals⁵³. Due to the fact that the diagonal blocks of the double excitation part are actually \pm identity matrices, the double excitation part of the τ vector simply corresponds to the elements of the double excitation part of the trial vector matrix,

$${}^{\text{ee}}\tau_{aibj}^{\text{SOPPA}} = {}^{\text{ee}}b_{aibj} \quad (99)$$

The expressions for the property gradients were already presented in Eqs. (40), (41), (48), and (49) and will not be repeated here, as they cannot be rewritten in a one-index transformed form.

Thus, the equations needed for a relativistic SOPPA implementation have been presented in Eqs. (40), (41), (48), (49), (87), (89), (94), and (96)–(99).

4 Discussion of implementation approach

In the following section a possible approach for an implementation of the four-component SOPPA equations in a code, in which RPA is already provided in a spin-orbital basis, will be outlined.

4.1 Single excitation part of σ vector

For constructing the single excitation part of the σ vector in Eqs. (78), (87), (94), and (96), one can consider four different types of terms. First, the RPA contribution given by Eq. (94), which should be already provided by the program and hence will not be discussed further here. Second and third, the contributions in (96) that contain the MP1-amplitudes and the one-index transformed Fock matrix, respectively, and fourth the terms in Eq. (87).

The first two terms of Eq. (96) will require the one-index transformed two-electron integrals in the molecular orbital (MO) basis and the MP1-amplitudes. It should be possible to compute the MP1-amplitudes using existing code, as most quantum chemistry codes will be capable of running MP2-calculations. Likewise, it should be possible to obtain the two-electron integrals in the MO basis. If these are read into memory such that two indices are kept fixed while the remaining two are not, one can perform the one-index transformation by multiplying the appropriate block of the integral matrix, i.e., virtual-virtual, occupied-virtual, etc., with the trial vectors and then adding them as shown in Eq. (96). This is illustrated in Algorithm 1 lines 4–7 and 13–15, where the two outer loops are over the two indices that are kept fixed. The transformed integrals must then be multiplied with the appropriate MP1-amplitudes, as seen in lines 8–11 and 16–17 in Algorithm 1. Here, one must take care to keep any index, which is fixed for the integral matrix, also fixed for the amplitudes (see lines 9–10). In the case of two fixed amplitude indices, the matrix multiplication is straightforward (see lines 16–17). In the case of only one fixed amplitude index, it is more complicated. Consider the term $\sum_{cdk} \tilde{g}_{ackd} t_{ki}^{cd}$ in Eq. (96) for the fixed indices a and

c. Here, the transformed integral matrix will have dimension $k \times d$ (or occupied \times virtual), while the amplitude matrix will have dimension $d \times (k \times i)$. By multiplying the two matrices, the sum over index d is performed (line 8 in Algorithm 1). The resulting product will be of dimension $k \times (k \times i)$. However, the condition that the k index of the integrals and the k index of the amplitudes are the same must be fulfilled (see lines 9–10). Thus, by adding all elements for which index k of the integrals and index k of the amplitudes are the same, we obtain the elements of the σ vector for the fixed index a of the integrals and all values of the second index i of the amplitudes. Note that this sum is the sum over index k . To obtain the last sum over c , one must add all contributions of the σ vector obtained in this way with different fixed values of index c , i.e., in the second of the two outer loops in Algorithm 1.

The last two terms of Eq. (96) could be computed by multiplying the one-index trans-

Algorithm 1 Pseudocode illustrating the construction of the $\sum_{cdk} \tilde{g}_{ackd} t_{ki}^{cd}$ contribution to the σ vector.

```

1: for  $p = 1, N_{\text{orbs}}$  do                                 $\triangleright$  Summing index  $a$  OR index  $k$  in this illustration
2:   for  $q = 1, N_{\text{orbs}}$  do                                 $\triangleright$  Summing index  $c$  OR index  $d$  in this illustration
3:     if  $p$  and  $q$  virtual, i.e.,  $a = p$  and  $c = q$  then
4:                                      $\triangleright$  The sums are over indices  $a$  and  $c$ 
5:       for  $j = 1, N_{\text{occ}}$  do                                 $\triangleright$  Partial one-index transformation
6:          $(ac | k\tilde{d})+ = (ac | kj)b_{jd}$ 
7:       for  $b = 1, N_{\text{virt}}$  do                                 $\triangleright$  Partial one-index transformation
8:          $(ac | \tilde{k}d)+ = (ac | bd)b_{bk}$ 
9:       for  $d = 1, N_{\text{virt}}$  do                                 $\triangleright$  Sum index  $d$  now
10:        for  $k_{\text{amp}}=1, N_{\text{occ}}$  do  $\triangleright$  Neither  $k$  nor  $d$  were fixed, we need to sum  $k$  too
11:          if  $k$  .eq.  $k_{\text{amp}}$  then  $\triangleright$  Check the same index  $k$  to get sum
12:             $(ac | \tilde{k}d)t_{ki}^{cd}+ = (ac | \tilde{k}d)t_{k_{\text{amp}}i}^{cd} - (ac | kd)t_{k_{\text{amp}}i}^{cd}$ 
13:          else  $p$  occupied and  $q$  virtual i.e.  $k = p$  and  $d = q$ 
14:                                      $\triangleright$  Sums are over indices  $k$  and  $d$ 
15:            for  $j = 1, N_{\text{occ}}$  do                                 $\triangleright$  Partial one-index transformation
16:               $(kd | a\tilde{c})+ = (kd | aj)b_{jc}$ 
17:               $(kd | \tilde{a}c)+ = (kd | jc)b_{aj}$ 
18:            for  $c = 1, N_{\text{virt}}$  do                                 $\triangleright$  Sum over index  $c$ 
19:               $(kd | \tilde{a}c)t_{ki}^{cd}+ = (kd | \tilde{a}c)t_{ki}^{cd} - (kd | a\tilde{c})t_{ki}^{cd}$ 
20:           $\sum_{cdk} \tilde{g}_{ackd} t_{ki}^{cd}+ = (kd | \tilde{a}c)t_{ki}^{cd} + (ac | \tilde{k}d)t_{ki}^{cd}$ 

```

formed Fock matrix with the occupied-occupied part of the second-order contribution to the

density matrix and then adding the product of the virtual-virtual part of the second-order contribution to the density matrix and the one-index transformed Fock matrix. If RPA is already implemented, then a routine might already exist for the construction of the one-index transformed Fock matrix and thus one might reuse it or modify the routine to write the matrix to file for later use in the SOPPA calculation. Next, the second-order contribution to the density matrix should be computable using existing code and could therefore also be calculated using existing routines.

In order to compute the contributions given in Eq. (87), the two electron integrals will be required once more. Here, it will most likely be advantageous again to keep two indices fixed at a time in order to determine which of the trial vector elements should be added before multiplication of the integral matrix and the trial vectors takes place.

The sum of these new contributions should be added to the existing RPA σ vector and the existing routine for solving the RPA problem could then be used to solve the single excitation part of the SOPPA equations.

4.2 Double excitation part of σ vector

The double excitation part of the σ vector is determined from Eq. (79). To obtain the contributions given in Eq. (97), one has to perform the one-index transformations again by multiplying two-electron integrals and trial vectors and then adding them.

The contributions given in Eq. (89) will require the Fock matrix, which can be computed (or reused) by means of existing routines. The trial vectors must be added, potentially by keeping two indices (other than the one summed over) fixed at a time before multiplying with the Fock matrix.

4.3 τ vector

The single excitation part of the τ vector in Eq. (98) can be constructed by adding the second-order contribution to the existing RPA τ vector. To obtain this contribution, the virtual-

virtual part of the second-order contribution to the density matrix should be multiplied with the trial vector and subtracted from the product of the occupied-occupied part of the second-order contribution to the density matrix and the trial vector. The elements of the double excitation part of the τ vector given in Eq. (99) are (to a sign) simply the elements of the trial vector and can be constructed on the fly.

4.4 Property gradients

In case of solving the inhomogeneous set of equations given in Eq. (7) rather than the eigenvalue problem, the property gradients must also be constructed. For the single excitation part, Eqs. (48) and (49), one will once again require the second-order contribution to the density matrix as well as the integrals of the property operators in the MO basis. Routines should exist in any quantum chemistry code to compute these and multiplications can then be performed straightforwardly using the appropriate blocks of the matrices, i.e., the occupied-occupied block of the property integral matrix and the virtual-occupied block of the second-order contribution to the density matrix.

For the double excitation part, a matrix containing the property integrals in the MO basis will be required as well as the MP1-amplitudes. These must be multiplied, potentially by keeping two indices of the amplitudes fixed at a time.

5 Concluding remarks

The SOPPA method has proven its value in non-relativistic calculations, in particular for simulation of NMR.⁶ However, NMR of molecules with heavy elements cannot be reliably determined with non-relativistic methods^{30–34}. To overcome this problem, the SOPPA equations have been derived in a spin-orbital basis for an implementation in a four-component or two-component relativistic code. The equations required for a four-component SOPPA have been one-index transformed and are thus in a form suitable for efficient implementation.

They were derived in a basis of non-canonical spin-orbitals/spinors and are thus given in their most general form.

Our formulation in a non-canonical spin-orbital basis also allows for a non-relativistic implementation of SOPPA for open shell molecules and to significantly reduce computational costs for larger molecules by using localized occupied and virtual orbitals and exploiting Cholesky or resolution of identity techniques for the two-electron integrals in the MO basis. Moreover, a possible scheme has been outlined for an implementation of the presented equations in a program that already contains an RPA code that allows for the evaluation of the non-canonical RPA equations in a spin-orbital basis. This will allow spectroscopic properties of molecules containing heavy elements to be determined and greatly aid efforts to advance the understanding of spectroscopic experiments in order to develop new technologies.

6 Acknowledgements

SPAS thanks the VILLUM Foundation for a blokstipendium and EF gratefully acknowledges the VILLUM Foundation for a Villum Postdoc.

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PLEASE CITE THIS ARTICLE AS DOI:10.1063/1.50002389

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